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Small scale structured $BaTiO_3$-based coatings for catalytic applications

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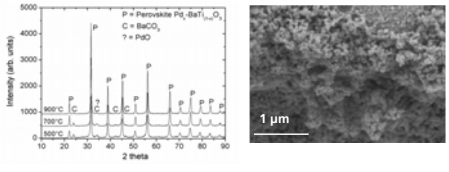
"Materials for harsh environments" and the "7. Materials day at Ruhr-University Bochum"

Introduction

Integration of precious metal in perovskite structures ($BaTi_{0.95}M_{0.05}O_3$, M = Pd, Rh, etc) results in more ageing resistance and higher N_2-selectivie catalysts compared to the precious metals supported on single oxides under temperatures exceeding 800°-900°C [1]. Homogeneous dispersed ion metals (i.e. Pt, Pd, Rh) in perovskite structures can result in more active and selective active sites as well. Here a Ba-based perovskite is prepared starting from different synthesis routes and doped with Pd and Rh. The catalytic properties of Rh and Pd-integrated perovskite are studied.

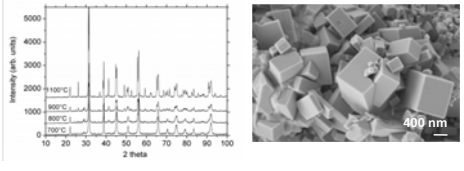
Sol-gel synthesis of Ba-based perovskite

$BaTi_{(1-x)}Pd_xO_3$ powder, using metallic Ba, Ti-isopropoxide and $Pd(NO_3)$



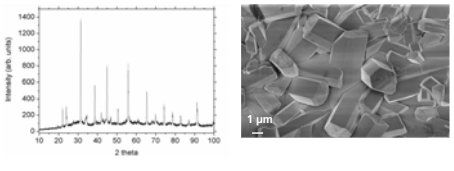
- Pd-substituted $BaTiO_3$-perovskite crystallizes at 500°C
- Traces of $BaCO_3$ present even after calcination at 900°C,

$BaTi_{(1-x)}Rh_xO_3$ powder, using $Ba(NO_3)$ $Rh(NO_3)$ and Ti-isopropoxide



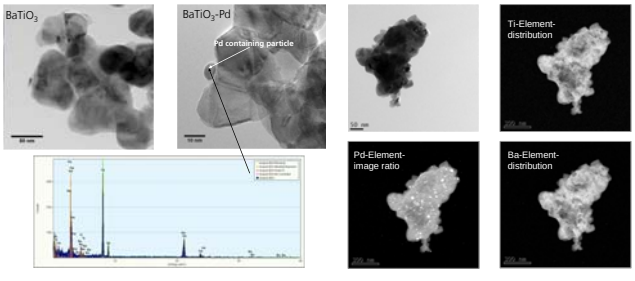
- Crystallization of cubic $BaTiO_3$ at 700°C,
- Rhombohedral and hexagonal $BaTiO_3$, with traces of BaO after 700°C,

$BaTiO_3$ coating on Ti-substrates, using $Ba(CO)_3$ and Ti-isopropoxide



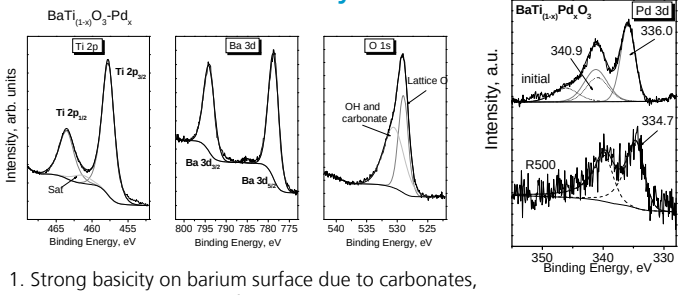
- $BaTiO_3$ coatings on Ti substrates,
- Crystallization of $BaTiO_3$ at 160°C

TEM and EDX analysis for identification of precious metal



1. Homogeneous distribution of Palladium in the perovskite matrix ,
2. Visualization difficulty due to none contrast between $BaTiO_3$-matrix and Pd-particles,
3. EF-TEM method allows the identification of Pd-particle in sizes of 5-15 nm,

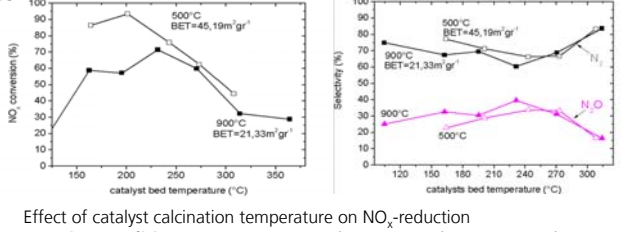
XPS analysis



1. Strong basicity on barium surface due to carbonates,
3. Ti-enrichment at the surface upon reduction treatment at 200°C,
4. The asymmetric lines for palladium indicate the presence of multiple ionic species, i.e. Pd intra-crystalline, Pd^{2+}, Pd^0,

H_2-Selective Catalytic Reduction of NO_x NO_x-conversion and N_2-selectivity

$BaTi_{(1-x)}Pd_xO_3$

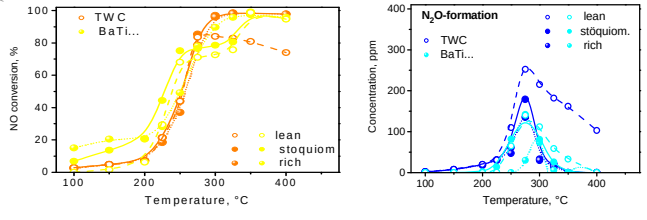


Effect of catalyst calcination temperature on NO_x-reduction
Reaction conditions: 720 ppm NO,1 vol. % H_2, 5 vol. % O_2, 7.2 vol. % H_2O and 7.2 vol. % CO_2, He as balance gas, SV = 55 200 hr^{-1}

$2NO + 4H_2 + O_2 \rightarrow N_2 + 4H_2O$,
(2) $2NO + 3H_2 + O_2 \rightarrow N_2O + 3H_2O$ [2]

NO + CO reaction NO_x-conversion and N_2O formation

$BaTi_{(1-x)}Rh_xO_3$



Effect of reaction temperature on NO_x-reduction
Reaction conditions:
Lean: 8500 ppm O_2
Stoichiometric:: 1,1 % CO, 1000 ppm Propen, 1000 ppm NO, 9500 ppm O_2, He balance
Rich: 10500 ppm O_2

Conclusions and outlook

- Formation of crystal phase(s) from $BaTiO_3$ perovskite sols is strongly influenced by the applied synthesis route,
- Hexagonal-shaped $BaTiO_3$-crystals grow on dip-coating of metallic substrates with modified $BaTiO_3$-sol at temperatures as low as 160°C,
- Pd or Rh can be integrated into $BaTiO_3$ perovskite by sol-gel route,
- XPS indicates that Pd-states corresponding to both PdO and Pd intra-crystalline (Pd^{3+}) are present in $BaTiPdO_3$,
- It is a challenging task to identify Pd in $BaTiO_3$ matrix (due to non-conductivity of the sample, size of the Pd-particles, Pd-ions in the crystal or on the perovskite surface). These problems were overcome by applying the energy filtering TEM working method,
- Pd and Rh integrated $BaTiO_3$ are promising catalysts for NO_x-reduction under rich and lean conditions; $BaTiPdO_3$ yields 80 to 90 % of NO_x-reduction and ca. 80 % selectivity to N_2 at 200°C under H_2-SCR conditions, $BaTi_{(1-x)}Rh_xO_3$ is very active between 100° and 200°C under rich conditions for NO reduction over CO + NO reaction.

References: [1] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Kimura, T. Okamoto and H. Hamada, Nature 418, 164-167 (2002).
[2] F. Dhainaut, S. Pietrzyk, P. Granger, Catal. Today 119 (2007) 94-99.

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